

## 5. POTENTIAL FOR HUMAN EXPOSURE

### 5.1 OVERVIEW

Methylene chloride has been identified in at least 882 of the 1,569 hazardous wastes sites that have been proposed for inclusion on the EPA National Priorities List (NPL) (HazDat 1999). However, the number of sites evaluated for methylene chloride is not known. The frequency of these sites can be seen in Figure 5-1. Of these sites, 882 are located in the United States, and none are located in the Commonwealth of Puerto Rico (not shown).

Methylene chloride is a widely used industrial chemical with reported emissions to air of more than 40 million pounds annually in the United States. Most of the methylene chloride released to the environment will partition to the atmosphere, where it will degrade with a lifetime of 6 months by reaction with photochemically produced hydroxyl radicals (WHO 1996). The compound is expected to be highly mobile in soil and to volatilize rapidly from surface water to the atmosphere. Biodegradation may be important, but bioconcentration does not appear to be significant.

The principal route of exposure for the general population to methylene chloride is inhalation of ambient air. Average daily intake of methylene chloride from urban air has been estimated to range from about 33 to 309  $\mu\text{g}$ . Occupational and consumer exposure to methylene chloride in indoor air may be much higher, especially from spray painting or other aerosol uses.

### 5.2 RELEASES TO THE ENVIRONMENT

According to the Toxics Release Inventory (TRI), in 1998, a total of about 41 million pounds (18.6 million kg) of methylene chloride was released to the environment from 714 facilities (714 facilities reported environmental releases of methylene chloride to TRI, another 113 facilities reported no releases at all for a total of 827 facilities) (TRI98 2000). This total release volume is approximately 10% of the total reported for 1997 (TRI97 1999). Table 5-1 lists amounts released from these facilities. In addition, an estimated 0.37 million pounds (0.17 million kg) were released by manufacturing and processing facilities to publicly owned treatment works (POTWs) or other off-site facilities (TRI98 2000). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

**Table 5-1. Releases to the Environment from Facilities that Manufacture or Process Methylene Chloride**

State <sup>b</sup>	Number of facilities	Total reported amounts released in pounds per year <sup>a</sup>					Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	Total on and Off-site release
		Air <sup>c</sup>	Water	Land	Underground injection				
AL	14	948907	0	0	0	948907	470	949377	
AZ	6	65837	0	0	0	65837	0	65837	
AR	12	125869	12	0	360837	486718	269	486987	
CA	44	986871	3	0	0	986874	9768	996642	
CO	6	37077	0	0	0	37077	0	37077	
CT	31	784114	755	3	0	784872	7450	792322	
DE	2	4100	0	0	0	4100	0	4100	
FL	16	932255	0	0	0	932255	759	933014	
GA	31	973595	1160	169543	0	1144298	14935	1159233	
IL	45	1745258	57	0	0	1745315	3295	1748610	
IN	47	4630842	639	5	0	4631486	1152	4632638	
IA	13	1156800	0	5	0	1156805	500	1157305	
KS	12	288373	0	0	41323	329696	1799	331495	
KY	15	2157130	57	0	0	2157187	11435	2168622	
LA	11	41136	1020	0	9954	52110	2236	54346	
ME	1	3394	0	0	0	3394	0	3394	
MD	5	118361	0	0	0	118361	0	118361	

**Table 5-1. Releases to the Environment from Facilities that Manufacture or Process Methylene Chloride  
(continued)**

State <sup>b</sup>	Number of facilities	Total reported amounts released in pounds per year <sup>a</sup>						
		Air <sup>c</sup>	Water	Land	Underground injection	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	Total on and Off-site release
MA	29	139895	0	0	0	139895	4772	144667
MI	32	422374	177	0	54800	477351	1954	479305
MN	17	183564	290	0	0	183854	0	183854
MS	15	3355695	0	0	0	3355695	900	3356595
MO	26	302907	110	5	0	303022	0	303022
MT	1	42300	0	0	0	42300	0	42300
NE	3	41152	0	0	0	41152	2085	43237
NV	2	6834	0	0	0	6834	0	6834
NH	3	38696	0	0	0	38696	40	38736
NJ	35	243166	548	3	0	243717	5977	249694
NM	1	105	0	0	0	105	0	105
NY	24	2038566	4305	0	0	2042871	29091	2071962
NC	29	2599415	4271	450	0	2604136	750	2604886
OH	54	1864209	257	0	0	1864466	21070	1885536
OK	12	250064	0	0	0	250064	32	250096
OR	7	79509	0	0	0	79509	2987	82496

**Table 5-1. Releases to the Environment from Facilities that Manufacture or Process Methylene Chloride  
(continued)**

State <sup>b</sup>	Number of facilities	Total reported amounts released in pounds per year <sup>a</sup>						
		Air <sup>c</sup>	Water	Land	Underground injection	Total on-site release <sup>d</sup>	Total off-site release <sup>e</sup>	Total on and Off-site release
PA	36	3545433	37	0	1	3545471	47945	3593416
PR	18	2441482	0	0	0	2441482	7555	2449037
RI	2	18677	0	0	0	18677	0	18677
SC	22	1934986	1050	12127	0	1948163	6020	1954183
TN	26	2738055	0	0	0	2738055	17200	2755255
TX	54	822273	567	1990	23749	848579	110891	959470
UT	7	56753	0	0	0	56753	8376	65129
VA	20	1412207	0	5	0	1412212	422	1412634
WA	14	176129	294	176	0	176599	45145	221744
WV	5	67789	147	38	0	67974	0	67974
WI	22	565148	0	0	0	565148	0	565148
Total	827	40387302	15756	184350	490664	41078072	367280	41445352

Source: TRI98 2000

<sup>a</sup>Data in TRI are maximum amounts released by each facility.

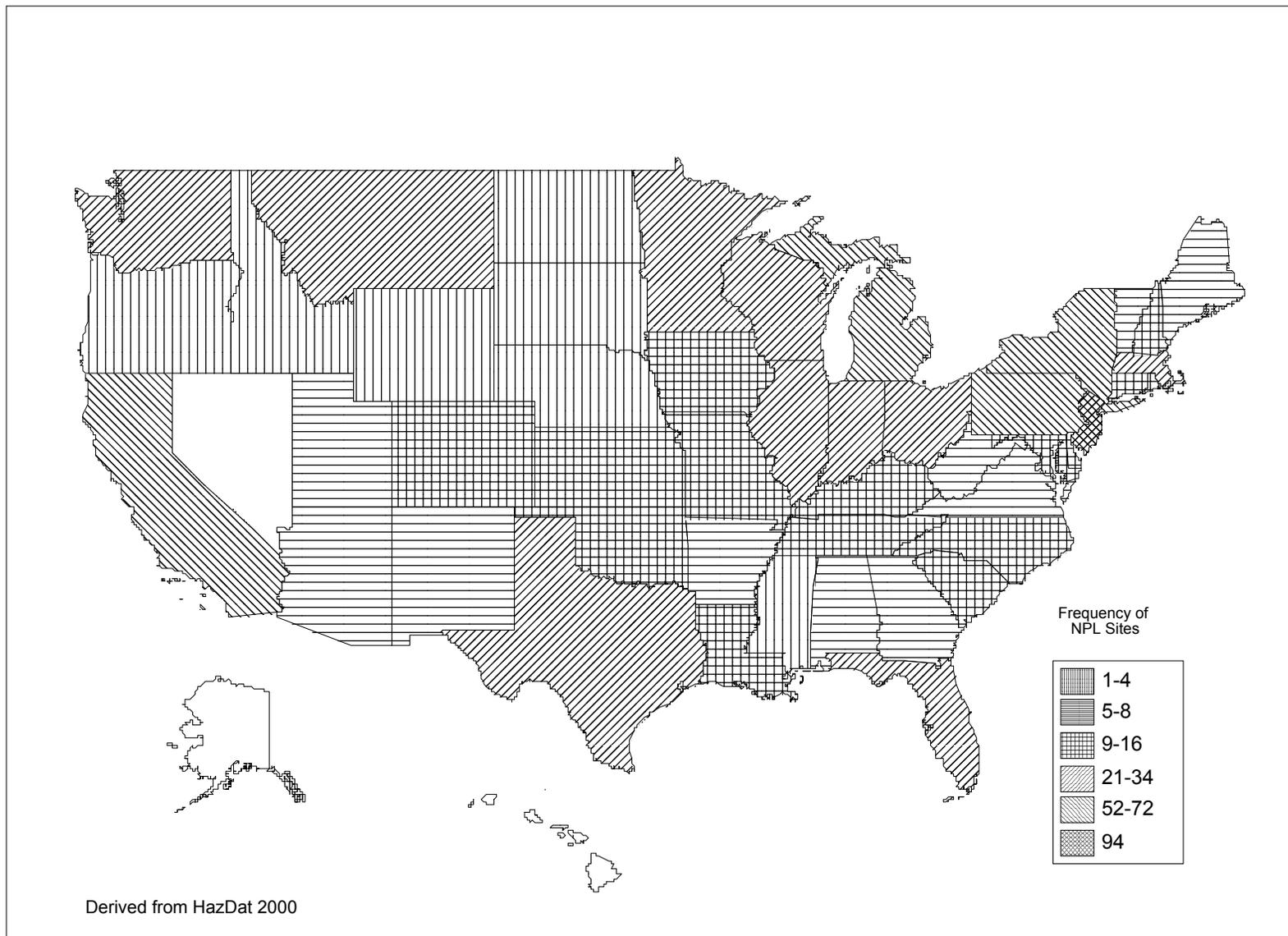
<sup>b</sup>Post office state abbreviations are used.

<sup>c</sup>The sum of fugitive and stack releases are included in releases to air by a given facility.

<sup>d</sup>The sum of all releases of the chemical to air, land, water, and underground injection wells.

<sup>e</sup>Total amount of chemical transferred off-site, including to publicly owned treatment works (POTW)

Figure 5-1. Frequency of NPL Sites with Methylene Chloride Contamination



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Methylene chloride has been identified in a variety of environmental media (air, surface water, groundwater, soil, and sediment) collected at 882 of the 1,569 NPL hazardous waste sites (HazDat 1999).

**5.2.1 Air**

According to the Toxics Release Inventory, in 1998, the estimated releases of methylene chloride of 40 million pounds (18.3 million kg) to air from 714 large processing facilities accounted for about 97.4% of total environmental releases (TRI98 2000). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Methylene chloride has been identified in air samples collected at 108 of the 1,569 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1999).

Because methylene chloride is a highly volatile substance, most environmental releases are into the atmosphere. Methylene chloride is released to the atmosphere during its production, storage, and transport, but most (more than 99%) of the atmospheric releases result from industrial and consumer uses (EPA 1983c, 1985e). In 1992, 32.5% of the total global emission of methylene chloride was attributed to North America (McCulloch and Midgley 1996). It has been estimated that 85% of the total amount of methylene chloride produced in the United States is lost to the environment (EPA 1985e), about 86% of which is released to the atmosphere (EPA 1982a). Thus, about 73% (370 million pounds) of the U.S. production volume for 1988 (500 million pounds), of methylene chloride was lost to the atmosphere in 1988. Manufacturers, processors, and users of methylene chloride are required to report the quantities of methylene chloride released to environmental media or transferred to off-site disposal facilities annually (EPA 1998j). The data currently available, compiled in the Toxics Release Inventory (TRI98 2000), are for releases in 1998 and are summarized in Table 5-1. Methylene chloride was the 14<sup>th</sup>-largest release and transfer chemical reported in the United States for 1988 (EPA 1990c). The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Industrial methylene chloride emissions to the atmosphere reported to EPA for the 1988 TRI totaled about 127 million pounds (TRI88 1990). Emissions from the use of consumer products and other sources such as hazardous waste sites may be estimated to be 243 million pounds by subtracting industrial emissions (127 million pounds) from total atmospheric loss of methylene chloride (370 million pounds). Consumer

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products containing methylene chloride in wide use include paint strippers, aerosols, adhesives and glues, and cleaning fluids and degreasers (CPSC 1990). Virtually all the methylene chloride in these products is released to the atmosphere during use. Its use in hair sprays was banned in 1989 by the FDA (1989).

Methylene chloride is formed during water chlorination (NAS 1977) and is emitted to the air from waste waters in treatment plants (Corsi et al. 1987; Dunovant et al. 1986; Namkung and Rittmann 1987). Methylene chloride emissions from treatment plants in California are estimated to exceed 400,000 pounds annually (Corsi et al. 1987). Declining production amounts of methylene chloride will result in a decrease in the volume emitted to the atmosphere.

**5.2.2 Water**

According to the Toxics Release Inventory, in 1998, the estimated releases of methylene chloride of about 15,756 pounds (7,090 kg) to water from 714 facilities accounted for < 0.04% of total environmental releases (TRI98 2000). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Methylene chloride has been identified in surface water and groundwater samples collected at 633 and 218, respectively, of the 1,569 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1999).

About 2% of environmental releases of methylene chloride are to water (EPA 1982a). Industrial releases of methylene chloride to surface water and underground injection (potential groundwater release) reported to the TRI in 1998 totaled 506,420 pounds (TRI98 2000). Methylene chloride has been identified in industrial and municipal waste waters from several sources at concentrations ranging from 0.08 ppb to 3,400 ppm (Dunovant et al. 1986; EPA 1979a, 1982a; Namkung and Rittmann 1987). It has also been reported in the leachate from industrial and municipal landfills at concentrations from 0.01 to 184 ppm (Brown and Donnelly 1988; Sawhney 1989). The levels of methylene chloride in surface water have been reported to vary from nondetectable to 10 ppb (California Environmental Protection Agency 1992).

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Methylene chloride has been detected in both surface water and groundwater samples taken at hazardous waste sites. Data from the Contract Laboratory Program (CLP) Statistical Database indicate methylene chloride was found at geometric mean concentrations of 68 and 98 ppb in surface water and groundwater samples, respectively, at about 30% of the sites sampled (CLPSD 1990). Note that the information used from the CLP Statistical Database includes data from both NPL and non-NPL sites.

### 5.2.3 Soil

According to the Toxics Release Inventory, in 1998, the estimated releases of methylene chloride of about 184,350 pounds (82,958 kg) to soil from 714 facilities accounted for about <0.44% of total environmental releases (TRI98 2000). Table 5-1 lists amounts released from these facilities. The TRI data should be used with caution because only certain types of facilities are required to report. This is not an exhaustive list.

Methylene chloride has been identified in soil (412 sites) and sediment (179 sites) samples collected at the 1,569 NPL hazardous waste sites where it was detected in some environmental media (HazDat 1999). The principal sources of methylene chloride releases to land are disposal of methylene chloride products and containers to landfills. Substantial reduction to industrial disposal of methylene chloride to the land is likely since the inception of the Land Disposal Restrictions (EPA 1998c). However, disposal of containers for consumer products containing residues of methylene chloride may continue to occur. It is estimated that about 12% of methylene chloride losses to the environment are to land (EPA 1982a).

Methylene chloride has been detected in soil/sediment samples taken at 36% of the hazardous waste sites included in the CLP Statistical Database at a geometric mean concentration of 104 ppb (CLPSD 1990).

## 5.3 ENVIRONMENTAL FATE

### 5.3.1 Transport and Partitioning

Methylene chloride is a volatile liquid, with a boiling point of 40 EC (Lide 1994) and a vapor pressure of 349 mm Hg at 20 EC (Verschuere 1983). Therefore, methylene chloride tends to volatilize to the atmosphere from water and soil. The half-life of methylene chloride volatilization from water has been

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found to be 21 minutes under experimental conditions (Dilling et al. 1975), but actual volatilization from natural waters will depend on the rate of mixing, wind speed, temperature, and other factors (Dilling et al. 1975; EPA 1979b). The Henry's law constant value (H) of 0.002 atm/m<sup>3</sup>/mol (EPA 1982e; Gossett 1987) indicates that methylene chloride will volatilize rapidly from moist soil and water surfaces (Thomas 1990).

Methylene chloride is not strongly sorbed to soils or sediments (Dilling et al. 1975; Dobbs et al. 1989). Based on its low soil organic carbon partitioning coefficient ( $K_{oc}$ ) of 25, methylene chloride is likely to be very highly mobile in soils (Bahnick and Doucette 1988; Roy and Griffin 1985) and may be expected to leach from soils into groundwater.

Based on a reported log octanol/water partition coefficient ( $K_{ow}$ ) of 1.3 (Hansch and Leo 1979), an estimated bioconcentration factor (BCF) of 2.3 was derived (EPA 1980a, 1984). There is no evidence of biomagnification, but because the estimated BCF is low, significant biomagnification of methylene chloride in aquatic food chains is not expected.

### 5.3.2 Transformation and Degradation

#### 5.3.2.1 Air

The main degradation pathway for methylene chloride in air is its reaction with photochemically generated hydroxyl radicals (Cox et al. 1976; Crutzen and Fishman 1977; Davis et al. 1976; EPA 1980f, 1987i). Thus, the atmospheric lifetime of methylene chloride may be predicted from the hydroxyl radical concentration in air and the rate of reaction. Most reported rates for hydroxyl radical reaction with methylene chloride range from  $1.0 \times 10^{-13}$  to  $1.5 \times 10^{-13}$  cm<sup>3</sup>/mol/sec, and estimates of average atmospheric hydroxyl radical concentration range from  $2.5 \times 10^5$  to  $1 \times 10^6$  mol/cm<sup>3</sup> (Cox et al. 1976; Crutzen and Fishman 1977; Davis et al. 1976; EPA 1980f, 1985e, 1985g). Using this information, an average atmospheric lifetime for methylene chloride may be calculated to be 130 days. Other estimates range from 100 to 500 days (Altshuller 1980; Cox et al. 1976; Davis et al. 1976; EPA 1987i; Sidebottom and Franklin 1996). Because this degradation pathway is relatively slow, methylene chloride may become widely dispersed but is not likely to accumulate in the atmosphere. The small amount of methylene chloride which reaches the stratosphere (about 1%) may undergo direct photolytic degradation; however, photolysis in the troposphere is not expected (Howard et al. 1990). Reactions of methylene chloride with

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ozone or other common atmospheric species (e.g., oxygen atoms, chlorine atoms, and nitrate radicals) are not believed to contribute to its breakdown (EPA 1985g, 1987i; WHO 1996).

**5.3.2.2 Water**

Methylene chloride undergoes slow hydrolysis in water. The experimental half-life reported for the hydrolysis reaction, at neutral conditions, is approximately 18 months at 25 EC (Dilling et al. 1975). However, the rate of reaction varies greatly with changes in temperature and pH. A hydrolytic half-life of 14 days was reported for methylene chloride in acidic solutions at 80–150 EC (EPA 1979b, 1985e). This experimental value, when extrapolated to 25 EC, is about 700 years. Different mechanisms of hydrolyses may be responsible for these two widely different values.

Both aerobic and anaerobic biodegradation may be an important fate process for methylene chloride in water (Brunner et al. 1980; Davis et al. 1981; EPA 1985e; Stover and Kincannon 1983; Tabak et al. 1981). In the laboratory, methylene chloride can be biodegraded by aerobic bacteria such as *Methylobacterium* sp. and *Methylophilus* sp. and anaerobic bacteria such as *Hyphomicrobium* sp. and *Dehalobacterium* sp. (Leisinger et al. 1994; Magli et al. 1998). These bacteria are able to efficiently utilize methylene chloride as a carbon and energy source. The *Acinebacter* sp. has been shown to use oxygen or nitrate ion as the electron acceptor (Sheehan and Freedman 1996). Methylene chloride has been observed to undergo degradation at a rapid rate under aerobic conditions. Reported total methylene chloride loss was 100% after 7 days in a static culture flask biodegradability screening test (Tabak et al. 1981) and 92% after 6 hours in a mixed microbial system (Davis et al. 1981). Volatilization loss was not more than 25% (Tabak et al. 1981).

**5.3.2.3 Sediment and Soil**

Degradation of methylene chloride was found to occur in soils with concentrations ranging from approximately 0.1 to 5.0 ppm (Davis and Madsen 1991). The rate of biodegradation was found to be dependent on soil type, substrate concentration, and redox state of the soil. Methylene chloride biodegradation has been reported to occur under both aerobic conditions and anaerobic conditions (Davis and Madsen 1991). The biodegradation of methylene chloride appears to be accelerated by the presence of elevated levels of organic carbon (Davis and Madsen 1991).

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Methylene chloride has a low tendency to absorb to soil (Dilling et al. 1975; Dobbs et al. 1989); therefore, there is a potential for leaching to groundwater. Also, because of the high vapor pressure, volatilization to air is also a likely fate process from dry soil. Its high Henry's law constant (0.002 atm/m<sup>3</sup>/mol) indicates that volatilization from moist soil is also likely.

**5.4 LEVELS MONITORED OR ESTIMATED IN THE ENVIRONMENT**

Reliable evaluation of the potential for human exposure to methylene chloride depends in part on the reliability of supporting analytical data from environmental samples and biological specimens. In reviewing the data on methylene chloride levels monitored or estimated in the environment, it should also be noted that the amount of chemical identified analytically is not necessarily equivalent to the amount that is bioavailable. The analytical methods available for monitoring methylene chloride in a variety of environmental media are detailed in Chapter 6 (Analytical Methods).

**5.4.1 Air**

Methylene chloride has been detected in ambient air samples taken from around the world, as shown in Table 5-2. Background levels are usually at about 50 parts per trillion (0.17 µg/m<sup>3</sup>) (Singh et al. 1982). Methylene chloride was among the chemicals monitored in a statewide survey of hazardous air pollutants by the Arizona Hazardous Air Pollutants Monitoring Program. The average amount of methylene chloride detected in air ranged from 0.61 ppm on a hillside in Yavapai County to 1.62 ppm in Phoenix (Zielinska et al. 1998). Concentrations of methylene chloride in urban areas and in the vicinity of hazardous waste sites are generally one to two orders of magnitude higher. These values are all much lower than the concentrations which may be encountered inside buildings where products containing methylene chloride are being used (NAS 1978; Otson et al. 1983).

**5.4.2 Water**

Methylene chloride has been detected in surface water, groundwater, and finished drinking water throughout the United States. It was detected in 30% of 8,917 surface water samples recorded in the STORET database, at a median concentration of 0.1 ppb (Staples et al. 1985). In a New Jersey survey (Page 1981), methylene chloride was found in 45% of 605 surface water samples, with a maximum concentration of 743 ppb. Methylene chloride has also been identified in surface waters in Maryland

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**Table 5-2. Summary of Methylene Chloride Levels in Air**

Location	Concentration (ppb) <sup>a</sup>		Reference
	Maximum	Mean	
Background	No data	0.05	Singh et al. 1982
Oceanic:			
Northern Hemisphere	No data	10.37	Koppmann et al. 1993
Southern Hemisphere	No data	5.18	Koppmann et al. 1993
Rural/suburban United States	No data	0.05 <sup>c</sup> –0.60 <sup>c</sup>	EPA 1988d
Urban United States	22–200	0.23–1.93 <sup>b</sup>	EPA 1980e, 1988d; Harkov et al. 1984, 1985; Shikiya et al. 1984; Singh et al. 1982
Source dominated	No data	0.58 <sup>c</sup>	EPA 1988d
Hazardous waste sites	10–190	0.09–11.23 <sup>b</sup>	Harkov et al. 1985; La Regina et al. 1986
Indoor (nonresidential)	19,000	0.06–5,472 <sup>b</sup>	Harsch 1977; Otson et al. 1983

<sup>a</sup> 1 ppb = 3.47 µg/m<sup>3</sup>

<sup>b</sup> Range of values

<sup>c</sup> Median value

<sup>d</sup> Range of individual values

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(Helz and Hsu 1978), in Lakes Erie and Michigan (Konasewich et al. 1978), and at hazardous waste sites (Hauser and Bromberg 1982). Methylene chloride (0.2 ppm) was also detected in the shallow groundwater beneath Denver, Colorado (Bruce and McMahon 1996). Seawater also contains small amounts of methylene chloride; the mean reported concentration is  $2.2 \times 10^{-3}$  ppb (Singh et al. 1983).

Since volatilization is restricted in groundwater, concentrations of methylene chloride are often higher there than in surface water. Occurrence of methylene chloride in groundwater has been reported in several surveys across the United States, with concentrations ranging from 0 to 3,600 ppb (Dyksen and Hess 1982; EPA 1985h; Page 1981). Based on CERCLA records compiled during 1987, the compound was the sixth most frequently detected organic contaminant found in groundwater during hazardous waste disposal site investigations with a detection frequency of 19% (Plumb 1987).

Methylene chloride has been detected in drinking water supplies in numerous U.S. cities (Coleman et al. 1976; Dowty et al. 1975; EPA 1975b; Kool et al. 1982; Kopfler et al. 1977). Reported mean concentrations are generally less than 1 ppm (EPA 1975b). It was detected in 2.2% of 182 samples of bottled water surveyed with a mean concentration of positive samples at 0.059 ppb (Page et al. 1993). Water chlorination in treatment plants appears to increase both the concentration and the frequency of occurrence of methylene chloride in drinking water supplies (Bellar et al. 1974; EPA 1975b; NAS 1977).

#### 5.4.3 Sediment and Soil

No studies were located on methylene chloride levels in soil. However, methylene chloride was detected in 20% of 338 sediment samples recorded in the STORET database, at a median concentration of 13  $\mu\text{g}/\text{kg}$  (Staples et al. 1985).

#### 5.4.4 Other Environmental Media

Although methylene chloride is used in food processing (solvent extraction of coffee, spices, hops) and as a post-harvest fumigant for some foods (strawberries, grain), little information was located on levels in foods. Residual levels of methylene chloride in decaffeinated coffee beans ranging from 0.32 to 0.42 ppm were reported in the United States (IARC 1986), and levels ranging from 0.01 to 0.1 ppm were reported by a major coffee processor (FDA 1985). These levels are well within the FDA limits of 10 ppm for methylene chloride in decaffeinated coffee. Although the FDA considers residues at or below the

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FDA limit to be safe (FDA 1985), it has been reported that methylene chloride is no longer used as a decaffeinating agent by most coffee decaffeimators (Mannsville Chemical Products Corporation 1988). The FDA has also set a limit of 30 ppm for methylene chloride in spice oleoresins, but EPA has exempted methylene chloride from the requirement of a tolerance for fumigated food materials (see Chapter 7). Oysters and clams from Lake Pontchartrain in Louisiana had mean methylene chloride levels of 7.8 and 27 ppb, respectively (Ferrario et al. 1985).

**5.5 GENERAL POPULATION AND OCCUPATIONAL EXPOSURE**

Inhalation of methylene chloride from ambient air is the predominant route of exposure for the general population in the United States. As calculated by Singh et al. (1981), the average daily doses of methylene chloride from ambient air in three U.S. cities range from 33 to 309  $\mu\text{g}/\text{day}$ , based on 1979 monitoring data and a daily air intake of 23  $\text{m}^3$  by an adult. Since the amount of methylene chloride manufactured has recently dropped below the production levels of the late 1970s, average daily doses may currently be somewhat less than these values. Methylene chloride was detected in the blood of fewer than 10% of the 600 samples obtained from people who participated in the Third National Health and Nutrition Examination Survey (NHANES III) (Ashley et al. 1994). Inhalation exposure may also occur through the use of consumer products containing methylene chloride (CPSC 1987) (see Section 5.7).

Since concentrations of methylene chloride in water and food are generally quite low, it appears that exposure from sources other than air is unlikely to be important. For example, drinking water containing 1 ppb methylene chloride would provide an additional intake of 2  $\mu\text{g}$  per day for an adult drinking 2 L of water per day.

Methylene chloride has been identified, but not quantified, in eight out of eight samples of human breast milk collected in four urban areas in the United States (EPA 1980d; Pellizzari et al. 1982).

Occupational exposure to methylene chloride may be important in numerous industries. Workers may be exposed during the production and processing of methylene chloride. They may also be exposed to methylene chloride during a variety of industrial activities including spray painting, spray gluing, metal painting, paint stripping, and aerosol packing (IARC 1986; OSHA 1986; Whitehead et al. 1984). The NIOSH estimated that the number of workers exposed to methylene chloride increased from about

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1 million in the early 1970s to 1.4 million in the early 1980s (NIOSH 1986; NOES 1990). Since production and use of methylene chloride has decreased (as have threshold limit values) since the mid-1980s (see Sections 4.1 and 4.3), the number of workers exposed to methylene chloride has decreased accordingly.

Monitoring data for methylene chloride in workplace air from 1968 to 1982 indicate that concentrations in the general work area ranged from 0.086 to 964.8 ppm while samples in the breathing zone of workers ranged up to 1,411 ppm (IARC 1986). Installation of appropriate ventilation systems has been found to lower the workers' exposure to methylene chloride in the breathing zone from 600–1,150 ppm to 28–34 ppm (Estill and Spencer 1996). The current OSHA Permissible Exposure Limit (PEL) for methylene chloride for an 8-hour workday is 25 ppm (88.25 mg/m<sup>3</sup>) (OSHA 1997). An estimated 237,496 workers are potentially exposed while involved with methylene chloride manufacturing, paint manufacturing, metal cleaning, polyurethane foam manufacturing, plastics and adhesives manufacturing, ink use, pharmaceuticals, construction, and shipyards. The largest numbers of occupationally exposed individuals occur in areas of metal cleaning, industrial paint stripping, and ink solvent uses (OSHA 1997). The American Conference of Governmental Industrial Hygienists (ACGIH) reduced their Threshold Limit Value (TLV) (the recommended 8-hour exposure limit) from 100 to 50 ppm (174 mg/m<sup>3</sup>) in 1988 (ACGIH 1990), which continues to be the recommended TLV level (ACGIH 1998).

## 5.6 EXPOSURES OF CHILDREN

This section focuses on exposures from conception to maturity at 18 years in humans. Differences from adults in susceptibility to hazardous substances are discussed in 2.7 Children's Susceptibility.

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of adults. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults in avoiding hazards (NRC 1993).

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Young children often play close to the ground and frequently play in dirt, which increases their dermal exposure to toxicants in dust and soil. They also tend to ingest soil, either intentionally through pica or unintentionally through hand-to-mouth activity. Children, thus, may be orally and dermally exposed to methylene chloride present as a contaminant in soil and dust. It has been demonstrated that methylene chloride is rapidly absorbed by the skin (McDougal et al. 1986). Methylene chloride has a  $K_{oc}$  of 25, indicating a very low adsorption to soil (Bahnick and Doucette 1988; Roy and Griffin 1985; Swann et al. 1983). Most of the methylene chloride present in the upper layers of the soil will be rapidly volatilized to air (vapor pressure=349 mmHg at 20 EC). Loss of methylene chloride from the soil decreases the potential of dermal and oral exposure to children, but its rapid volatilization results in inhalation being the most likely route of exposure during play on the ground.

The higher ventilation rate in children compared to adults means that for a brief period, children will be more vulnerable than adults to acute neurological effects from short-term inhalation exposures. However, differences between children and adults are eliminated as steady-state concentrations are reached, i.e., within 2–4 hours (see Section 2.3.1.1). Thus, children would not be expected to be more vulnerable than adults in the case of intermediate- or chronic-duration exposures. Young children are closer to the ground or floor because of their shorter stature. The methylene chloride vapors being heavier than air (vapor density = 2.93) tend to concentrate near the ground. Children, therefore, are at a greater risk of exposure than adults during accidental spills or through indoor use of methylene chloride in an unventilated area.

Exposures of the embryo or fetus to volatile organic compounds such as methylene chloride may occur if the expectant mother is exposed. A newborn infant may be exposed by breathing contaminated air and by ingestion of mother's milk, which can contain small amounts of methylene chloride. Children may be exposed through accidental ingestion of products containing methylene chloride. Older children and adolescents may be exposed to methylene chloride in their jobs or hobbies, or through deliberate solvent abuse by "sniffing." Human epidemiological studies and case reports discussing reproductive and/or developmental toxicity of methylene chloride in humans have been reviewed. Exposure routes included occupational duties and sniffing of paint removers. Inhalant abuse during pregnancy poses significant risks to the pregnancy and endangers both the mother and the fetus. Solvent abuse of methylene chloride for euphoric effects results in exposure levels that equal or exceed those producing adverse effects in animals.

## 5. POTENTIAL FOR HUMAN EXPOSURE

There are no existing studies that have monitored the level of exposure from methylene chloride to children. Most uses of methylene chloride are associated with occupational purposes, so it is unlikely that children will receive significant doses. Under extreme conditions where paint thinners or other mixtures containing high concentrations of methylene chloride are used in the presence of children in an enclosed area with little or no ventilation, children could receive significant exposure. There are studies that examine the exposure to children from parents' work clothes, skin, hair, tools, or other objects removed from the workplace (NIOSH 1995); however, this type of "take home" or secondary exposure is unlikely due to the high volatility of methylene chloride. Additional exposure from consumer products can occur, but is unlikely to be significant, although little data are available at this time.

Methylene chloride has been identified, but not quantified, in eight out of eight samples of human breast milk collected in four urban areas in the United States (EPA 1980d; Pellizzari et al. 1982).

It is not known whether children differ in their weight-adjusted intake of methylene chloride. However, children drink more fluids per kilogram of body weight than adults (NRC1993) and methylene chloride has been detected in drinking water (Section 5.4.2).

## 5.7 POPULATIONS WITH POTENTIALLY HIGH EXPOSURES

In addition to individuals who are occupationally exposed to methylene chloride (see Section 5.5), there are several groups within the general population that could have potentially high exposures (higher than background levels) to methylene chloride. These populations include individuals living in proximity to sites where methylene chloride was produced or sites where methylene chloride was disposed, and individuals living near 1 of the 1,569 NPL hazardous waste sites where methylene chloride has been detected in some environmental media (HazDat 1996).

Individuals using consumer products containing substantial amounts of methylene chloride have the potential for high exposure to this compound (CPSC 1987). Paint strippers, adhesive removers, spray shoe polishes, adhesives, glues, paint thinners, and many other household products contain enough methylene chloride to expose consumers to significant amounts of methylene chloride vapor when the products are used, especially indoors (CPSC 1987, 1990). Indoor air concentrations resulting from the use of methylene chloride-containing consumer products have been estimated to range from 0.06 to 5,472 ppb (Callahan 1981; NAS 1978; Otson et al. 1983). Previous estimates indicated that a concentra

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tion of 50 ppm (174 mg/m<sup>3</sup>) of methylene chloride would have been expected in the breathing zone of consumers following hair spray use (FDA 1985), resulting in a time-weighted average exposure of 0.174 ppm. Hair care specialists would have been exposed to 10 times this level (FDA 1985). However, this source of exposure has been virtually eliminated since the FDA (1989) banned the use of methylene chloride in hairsprays.

Coffee drinkers who consume large amounts of decaffeinated coffee which has been extracted with methylene chloride may be exposed from this source. Assuming all the methylene chloride is extracted from the beans during brewing and none is volatilized (FDA 1985), the maximum daily intake for a person drinking 5 cups of decaffeinated coffee is about 12 µg, a fraction of intake from ambient air. Since volatilization during brewing is very likely, the actual intake is probably much lower. In addition, this source of exposure is becoming less important, since most decaffeination processes no longer use methylene chloride.

People living near industrial or hazardous waste sites with higher than average levels of methylene chloride in the air or water would have potential above-average exposure. However, the magnitude of this exposure can only be evaluated on a site-by-site basis.

Currently, workers in the industries identified above (Section 5.5) have the highest potential exposure to methylene chloride. OSHA has determined that a PEL TWA of 25 ppm substantially reduces significant risk of cancer from methylene chloride in occupational settings. OSHA also believes that a lower limit would further reduce risk and has set an action level measured as an 8-hour TWA to 12.5 ppm (OSHA 1997).

## 5.8 ADEQUACY OF THE DATABASE

Section 104(i)(5) of CERCLA, as amended, directs the Administrator of ATSDR (in consultation with the Administrator of EPA and agencies and programs of the Public Health Service) to assess whether adequate information on the health effects of methylene chloride is available. Where adequate information is not available, ATSDR, in conjunction with the National Toxicology Program (NTP), is required to assure the initiation of a program of research designed to determine the health effects (and techniques for developing methods to determine such health effects) of methylene chloride.

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The following categories of possible data needs have been identified by a joint team of scientists from ATSDR, NTP, and EPA. They are defined as substance-specific informational needs that if met would reduce the uncertainties of human health assessment. This definition should not be interpreted to mean that all data needs discussed in this section must be filled. In the future, the identified data needs will be evaluated and prioritized, and a substance-specific research agenda will be proposed.

**5.8.1 Identification of Data Needs**

**Physical and Chemical Properties.** Knowledge of the physical and chemical properties is essential for estimating the partitioning of the chemical and the fate in the environment. Information about the physical and chemical properties of methylene chloride is adequate (EPA 1982e; Hansch and Leo 1979; Lide 1994; Roy and Griffin 1982; Verschueren 1983) and can be used to determine the behaviors of the chemical. No further investigation is required.

**Production, Import/Export, Use, Release, and Disposal.** As of October 1, 1996, the International Trade Commission ceased to collect or publish annual synthetic organic chemicals data. The National Petroleum Refiners Association, which currently collects such data, does not include methylene chloride on its list of organic chemicals. The available production data for methylene chloride are out of date. It is essential that these data be updated regularly to allow a more accurate determination of the potential for human exposure.

Remedial investigations and feasibility studies at NPL sites that contain methylene chloride are needed to provide further information on environmental concentrations and human exposure levels near these sites.

According to the Emergency Planning and Community Right-to-Know Act of 1986, 42 U.S.C. Section 11023, industries are required to submit chemical release and off-site transfer information to the EPA. The Toxics Release Inventory (TRI), which contains this information for 1996, became available in May of 1998. This database will be updated yearly and should provide a list of industrial production facilities and emissions.

Data on the production and uses of methylene chloride in the United States are available (Mannsville Chemical Products Corporation 1988; NTP 1989; SRI 1999; TRI98 2000), however the parameters in which companies are monitored for the production of methylene chloride could be better characterized.

## 5. POTENTIAL FOR HUMAN EXPOSURE

Production of methylene chloride has decreased due to declining demands (HSDB 1990; Mannsville Chemical Products Corporation 1988; USITC 1989). Import/export data are available (Mannsville Chemical Products Corporation 1988; NTDB 1998) as well as data on land disposal (TRI98 2000), but more information is needed on disposal by incineration.

**Environmental Fate.** Methylene chloride is a highly volatile chemical and tends to volatilize from water and soil to the atmosphere (Dilling et al. 1975; EPA 1979b; Gossett 1987). The half-life of methylene chloride volatilization from water has been measured (Dilling et al. 1975). Methylene chloride does not strongly sorb to soils or sediments and can be expected to leach from soils to ground water (Dilling et al. 1975; Dobbs et al. 1989). Atmospheric lifetimes have been estimated from the reactions of methylene chloride with hydroxyl radicals and the concentration of such radicals (Altshuller 1980; Cox et al. 1976; Davis et al. 1976; EPA 1987i). Half-life values for the hydrolysis of methylene chloride in water has been reported (Dilling et al. 1975). Degradation of methylene chloride has been found to occur (Davis and Madsen 1991). Biodegradation of methylene chloride has been found to occur under both aerobic and anaerobic conditions (Leisinger et al. 1994; Magli et al. 1998; Sheehan and Freedman 1996). More information and data are needed for this process.

**Bioavailability from Environmental Media.** Data indicates the predominant route of exposure to methylene chloride is through inhalation (Angelo et al. 1986a; DiVincenzo et al. 1972). Studies also indicate the compound is readily absorbed following dermal exposure and ingestion (DiVincenzo and Kaplan 1981; McDougal et al. 1986; Stewart and Dodd 1964). Little information was found on levels of methylene chloride in food and no studies were found on the levels of methylene chloride in soil. Additional data on absorption in humans following ingestion and dermal exposures are needed to establish the importance of consumption of contaminated drinking water and foodstuffs and dermal contact with consumer products containing methylene chloride as exposure pathways for the general population.

**Food Chain Bioaccumulation.** The bioconcentration factor (2.3) estimated for methylene chloride is low (EPA 1980a, 1984). More data is needed on the bioaccumulation of methylene chloride by plants, aquatic organisms, and animals, and the biomagnification of methylene chloride in terrestrial and aquatic food chains. Data on bioaccumulation and biomagnification would aid in determining if levels of methylene chloride in the environment affect food chains and potentially impact human exposure.

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**Exposure Levels in Environmental Media.** Studies are available documenting levels of methylene chloride in air (EPA 1988d; Harkov et al. 1984; Otson et al. 1983; Singh et al. 1982), water (Dyksen and Hess 1982; EPA 1975b, 1985h; Page 1981; Singh et al. 1983; Staples et al. 1985), and sediments (Staples et al. 1985). More information is needed regarding the levels of methylene chloride in soils and sediments since there is little information at this time. Since production and use of methylene chloride have decreased in recent years and are projected to continue the downward trend, it would be valuable to have recent data to better estimate current human exposure levels from these media. More information is needed on methylene chloride levels measured in food.

Reliable monitoring data for the levels of methylene chloride in contaminated media at hazardous waste sites are needed so that the information obtained on levels of methylene chloride in the environment can be used in combination with the known body burdens of methylene chloride to assess the potential risk of adverse health effects in populations living in the vicinity of hazardous waste sites.

**Exposure Levels in Humans.** Methylene chloride has been identified and quantified in human breast milk (EPA 1980d; Pellizzari et al. 1982). More data is needed to determine the levels of methylene chloride in blood, urine, and other tissues in the general population, particularly for populations living in the vicinity of hazardous waste sites that contain methylene chloride. This information is needed to establish levels of methylene chloride to which the general population has been exposed through contact with contaminated air, drinking water, and consumer products. This information is necessary for assessing the need to conduct health studies on these populations.

**Exposures of Children.** There are no studies monitoring the level of exposure of children to methylene chloride. This data gap requires future studies to determine the exposure of methylene chloride to children and if the significant exposures can be decreased by any means. Additional studies are needed to examine various exposure pathways that are unique to children. Studies are also needed to examine children's weight-adjusted intake of methylene chloride.

Despite their higher ventilation rate per kilogram of body weight compared to adults, children are not at a greater risk of inhalation exposure to methylene chloride, except, initially for acute exposures. Steady state considerations tend to eliminate the difference between children and adults after a short time (see Section 2.3.1.1). They also spend more time closer to ground because of their height. Methylene chloride vapors, being heavier than air, tend to concentrate closer to the ground, thereby increasing the

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risk for children. No data are available on the exposure of children to methylene chloride present in the air.

A study on usefulness of intervention methods in cases of inhalant abuse by pregnant women is required. More research is needed to rule out concomitant risk factors and to identify specific chemicals and patterns of use associated with adverse effects.

Child health data needs relating to susceptibility are discussed in 2.12.2, Identification of Data Needs: Children's Susceptibility.

**Exposure Registries.** No exposure registries for methylene chloride were located. This substance is not currently one of the compounds for which a subregistry has been established in the National Exposure Registry. The substance will be considered in the future when chemical selection is made for subregistries to be established. The information that is amassed in the National Exposure Registry facilitates the epidemiological research needed to assess adverse health outcomes that may be related to exposure to this substance.

### 5.8.2 Ongoing Studies

As part of the ongoing Third National Health and Nutrition Evaluation Survey (NHANES III), the Environmental Health Laboratory Sciences Division of the National Center for Environmental Health, Centers for Disease Control and Prevention, is analyzing human blood samples for methylene chloride and other volatile organic compounds. These data will give an indication of the frequency of occurrence and background levels of these compounds in the general population.

A number of ongoing research efforts may provide data regarding the potential for human exposure to methylene chloride. These projects are summarized in Table 5-3.

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**Table 5-3. Ongoing Studies on the Potential for Human Exposure to Methylene Chloride**

Investigator	Affiliation	Research Description	Sponsor
	Argonne National Laboratory, Lemont, IL	Destruction/conversion of hazardous waste chlorocarbons	EM
Smith, G.B.	New Mexico State University, Las Cruces, NM	Pollutant toxicity reduction through biodegradation	NIGMS
Anders, M.W.	University of Rochester, Rochester, NY	Metabolism and toxicity of halogenated hydrocarbons	NIEHS
Hemingway, R.W.	Forest Service, Pineville, LA	Knot VOCs	USDA, CRGO
Morra, M.J.	University of Idaho, Moscow, ID	Biotic and abiotic degradation of glucosinolates and halogenated hydrocarbons in soil	USDA, CRGO
Scow, K.M.	University of California, Davis, CA	Microbial biodegradation of organic chemicals in soil	USDA, CRGO
Cook, R.	TDA Research, Inc. Wheat Ridge, CO	Catalysts for the oxidation of chlorinated hydrocarbons	EPA
Dragan, A.	Dragan Engineering, Encino, CA	Biofiltration of volatile organic compounds emitted a industrial waste treatment	AF
Wijmans, J.G.	Membrane Technology and Research, Menlo Park, NJ	Recovery of liquid hazardous wastes from carbon adsorption steam regeneration streams	EPA
Pfefferle, W.	Precision Combustion, New Haven, CT	Catalytically stabilized thermal incineration	NSF
Bohn, M.S.	National Renewable Energy Laboratory, Golden, CO	Incineration of hazardous materials with carbonate salts	USDOE
Strand, S.E.	University of Washington, Seattle, WA	Using trees to remediate groundwaters contaminated with chlorinated hydrocarbons	
Bernhard, R.A.	University of California, Davis, CA	Isolation, identification, and significance of micro-organic constituents in foods	

AF = Air Force; EPA = Environmental Protection Agency; NIEHS = National Institute of Environmental Health Sciences; NIGMS = National Institute of General Medical Sciences; NSF = National Science Foundation; USDA, CRGO = U.S. Department of Agriculture, Competitive Research Grant Office; USDOE = U.S. Department of Energy

